

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
16 September 2004 (16.09.2004)

PCT

(10) International Publication Number
WO 2004/078336 A2

(51) International Patent Classification⁷: **B01J** (74) Agent: SCHUPFNER, Georg, U.; Müller, Schupfner & Gauger, Parkstrasse 1, 21244 Buchholz (DE).

(21) International Application Number: PCT/EP2004/002086 (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DK, DM, DZ, EC, EH, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, L, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 2 March 2004 (02.03.2004)

(25) Filing Language: English (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(26) Publication Language: English

(30) Priority Data: 103 09 367.2 3 March 2003 (03.03.2003) DE

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Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



A2

WO 2004/078336 A2

(54) Title: PROCESS FOR THE DEHYDRATION OF ALCOHOLS YIELDING α -OLEFINS

(57) Abstract: The present invention relates to a process for producing α -olefins by dehydration of alcohols in the presence of γ -alumina. Furthermore, this invention relates to the use of γ -alumina as a dehydration catalyst.

PROCESS FOR THE DEHYDRATION
OF ALCOHOLS YIELDING α -OLEFINS

5 The present invention relates to a process for producing α -olefins by dehydration of alcohols in the presence of γ -alumina. Furthermore, this invention relates to the use of γ -alumina as a dehydration catalyst.

Linear α -olefins are produced on a large scale for example by ethylene oligomerisation, Fischer-Tropsch synthesis or, as in the case of 1-hexene, by controlled trimerisation. The ethylene oligomerisation can be performed for example according to Ziegler by a two-stage process, i.e. by a building-up reaction using triethyl aluminium, followed by 'short-time high-temperature displacement' (termed ALFEN process), or by a single-stage high-temperature process with 15 triethyl aluminium catalysis.

Another process for producing α -olefins is the dehydration of alcohols, which has been described in detail for example by Knözinger, H., *Angew. Chem. (Applied Chemistry)*, *Int. Ed.*, vol. 7, 1968, no. 10, p. 791-805.

20 Short-chain linear α -olefins are especially employed as co-monomers for making polyethylene copolymers. High purity is essential for this use, particularly as regards the 1-olefins content, plus the lowest possible amount of impurities, such as internal, branched, or cyclic alkenes, and dienes or alkynes. It is known that few 25 ppm of impurities already result in rapid deactivation of the polymerisation catalyst. Owing to the small boiling-point difference of the double-bond isomers and structural isomers of the olefins, which makes splitting by distillation expensive, the α -selectivity of the dehydration step is most important.

30 By the term ' α -selectivity' as used herein is meant the ratio of the α -olefin formed to the total olefins formed, i.e. the total of α -olefins, internal, branched, and cyclic olefins.

35 Suitable alumina catalysts for this application comprise for example zinc- and zirconium-doped aluminas (cf. e.g. U.S. patent 4,260,845; EP patent 0 150 832-B1, respectively). The α -selectivity can also be improved by addition of bases, which, however, has an adverse effect on the reactivity. For example, base-doped alumina

catalysts, such as barium-doped alumina, require significantly higher temperatures than the corresponding undoped catalysts. Acidic aluminas can be used at considerably lower temperatures causing, however, more isomerisation reactions and hence a decrease in α -selectivity.

5

Furthermore, it is known that there are processes, wherein prior to use the bases are homogeneously mixed with the alcohol. German patent DE 39 15 493 C2 describes the improvement of α -selectivity in the dehydration of fatty alcohols on γ -alumina by addition of 20 to 300 ppm of ammonia. However, it is a disadvantage of said 10 process to add an additional component, namely ammonia, which later must be separated.

The commonly known processes of alumina-catalysed dehydration have the 15 disadvantage of poor α -selectivity obtained with the customary catalysts. The selectivity can be improved at the expense of the turnover or by costly modification of the catalyst or by addition of further substances, which later must be separated. Moreover, reaction temperatures of greater than 350°C are necessary in order to achieve a fairly good conversion.

20 It is, therefore, an object of the present invention to provide a process for producing α -olefins by dehydration of alcohols, which process yields a high α -selectivity and good conversion at a low reaction temperature of less than 350 °C, particularly 320 °C and lower, without addition of bases or acids or without catalyst doping. Another object of the present invention is to provide a novel 25 dehydration catalyst.

According to the present invention, the problem has been solved by a process for producing α -olefins by dehydration of alcohols in the presence of γ -alumina, wherein the alcohol is brought into contact with at least one γ -alumina having

30 - a pore volume of greater than 0.9 ml/g, preferably greater than 1.0 ml/g (measured in accordance with DIN 66133, contact angle 131°C),
- at least one pore radii maximum in the mesopores range (10 to 250 Å) from 20 to 90 Å, preferably 30 to 80 Å, and
- at least one additional pore radii maximum in the macropores range 35 (greater than 250 Å).

The dehydration is preferably carried out at temperatures in the range from 260 to 350 °C, most preferably from 280 to 320 °C. The preferred embodiments of the subject invention are set out in the subordinate claims or hereinbelow.

5 According to the invention, the preferable alcohols are comprised of linear or branched 1-alkanols having 4 to 14 carbon atoms. Examples of suitable 1-alkanols include 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol, 1-tetradecanol, 2-ethyl-1-hexanol, and 2-butyl octanol, of which 1-hexanol and 1-octanol are particularly preferred.

10 In addition to all- γ -phase alumina, catalyst blends composed of γ - and δ -phases may be used as well. The γ -alumina according to the invention is mostly comprised of the γ -phase, namely, more than 50 wt%, preferably more than 90 wt%, and it has a bimodal pore radii distribution comprising at least one pore radius maximum in the mesopores range (pore radius 10 to 250 Å) and one in the macropores range (pore radius > 250 Å) with a total pore volume of greater than 0.9 ml/g and an amount of mesopores of preferably greater than 0.6 ml/g (determined in accordance with DIN 66133 by the mercury intrusion method at a contact angle of 131°). At least one maximum of the mesopores radii distribution of the γ -alumina of the invention is in the range from 20 to 90 Å, preferably 30 to 80 Å, whereas the preferable maximum of the macropores is greater than 1,000 Å.

15 It is preferable to use alumina having an Al_2O_3 content of >99 wt%, which unlike the aluminas described in US 4,260,845 or EP 0 150 832-B1, is not doped with zinc or zirconium or other additives, a process-conditioned amount of zinc and zirconium of typically less than 10 ppm notwithstanding. It is furthermore preferable not to employ any other type of dehydration catalysts, including co-catalysts or active carriers.

20 30 An example of a typical composition of the catalysts of the invention is given in Table I hereinbelow.

Table I

	Catalyst Composition	PURAL™ KR 1
5	Al	wt% 53.6
	Si	ppm 553
	Ca	ppm 176
	Na	ppm 159
	Fe	ppm 156
10	Mg	ppm 78
	Ga	ppm 70
	Ti	ppm 14
	Pb	ppm 14
	Cr	ppm 11
15	K	ppm <10
	Li, Zr, B, Mo, Ni, Mn, Zn, Cu, Co	each ≤ 5 ppm

In principle, any commercially available γ -alumina catalyst can be employed for the dehydration of 1-alcohols, but their use is less advantageous, compared to the catalysts of the invention. The $\gamma\text{-Al}_2\text{O}_3$ -catalysts of the invention differ from conventional catalysts in their physical properties, such as surface, porosity, pore geometry, and chemical composition. The catalysts of the invention excel by their high pore volume of greater than 0.9 ml/g and pore radii distribution which is at least bimodal and has at least one maximum in the mesopores range from 30 to 80 20 \AA and one in the macropores range of preferably $>1,000 \text{ \AA}$, wherein the pore volume of the mesopores preferably makes up more than 40 % of the total pore volume, whereas independently thereof the pore volume of the macropores 25 preferably constitutes more than 20 %. In the dehydration of 1-alcohol the special combination of physical properties of this alumina surprisingly yields a crude product having a significantly higher α -selectivity with unimpaired conversion (cf. Table II).

The γ -alumina catalysts of the invention are different from the conventional catalysts usually employed for the dehydration of 1-alcohols yielding 1-olefins, 30 because they have been modified by the manufacturing method, especially with respect to their physical properties, such that they have turned out to be

surprisingly selective in the dehydration process, particularly as regards the purity of the desired 1-olefin.

5 The process of the invention is preferably carried out at a pressure ranging from 10 to 2,000 mbar. The high-porosity alumina is preferably employed for example in the form of beads, extrudate clippings, granules, or pellets. The dehydration is preferably carried out continuously, most preferably in a continuous tube reactor.

10 The process of the invention can be carried out for example as follows:

15 The preferably gaseous alcohol is passed preferably at 280 to 320 °C through a reactor, especially a tube reactor, packed with the alumina of the invention. Pressure and temperature are such that at the reaction conditions of choice the catalyst is not contacted by liquid, e.g. the higher-boiling ether, which may theoretically be formed as an intermediate during the reaction. The alcohol may optionally be mixed with inert gas, e.g. nitrogen. The alumina is present for the most part as a g-phase material, preferably in the form of granules, extrudate, or beads.

20 The reaction product is condensed, the aqueous phase is separated, and the organic phase is analysed by gas chromatography in order to examine the reaction. With the purpose of evaluating the catalyst activity, the reactor is operated at steady conditions until a constant composition/stationary state is reached. The organic phase obtained after phase separation is distilled and both the unreacted alcohol and the dialkyl ether formed can be recycled to the process. Alternatively, the alcohol/dialkyl ether mixture can be separated from the olefin/water mixture by condensation immediately after the reaction, followed by direct recycling to the process.

25 The dihexyl ether which is usually formed as a by-product during the reaction of 1-hexanol can be distilled off and recycled to the process. The compositions of the crude educts/products and the test conditions for various catalysts have been compiled in Table II .

30 PURAL™ KR1 granules and extrudates are exemplary of the high-porosity bimodal γ -aluminas of the invention. When comparing the α -selectivities at 300 °C and a feed rate of 2 ml/min, their remarkable superiority over the

Südchemie catalyst is obvious. This superiority is yet more evident at 325 °C. PURAL™ KR2, too, is a high-porosity γ -alumina, but with a monomodal pore radii distribution. The P 180 catalyst is a high-porosity alumina, but compared with the 5 catalyst of the invention, it has a considerably greater average pore radius in the mesopores range.

It has become apparent that the process for producing 1-hexene in the co-monomer mode utilising the alumina according to the invention is much more cost-effective. For 10 example, working-up of the crude product by distillation in order to obtain a 1-hexene content of > 99 % can be accomplished by means of a column with fewer separation stages. The turnover can be affected by temperature, feed quantity (MHSV), and catalyst bed length, but the α -selectivity decreases as the turnover increases.

15 Figure 1 shows the pore radii distributions of PURAL™ KR1 according to example 3 and of PURAL™ KR2 according to comparative example 4. The pore radii were determined by the Hg intrusion method according to DIN 66133 at a contact angle of 131° using a measuring apparatus of *micromeritics* company.

20 Figure 2 shows the 1-hexene content in the crude product versus the α -selectivity as a function of feed quantity and temperature. The data points plotted for a 1-hexene content of less than 30 % have been obtained at 300 °C, whereas the data collected for a 1-hexene content of greater than 30 % are based on 325 °C (legend: (1) 300°C, 2 ml/min; (2) 325°C, 3 ml/min; (3) 325°C, 2 ml/min; (4) 325°C, 1 25 ml/min). With an increasing turnover the differences in the α -selectivities of various catalysts become particularly plain.

Examples

30

Preparation of γ -Al₂O₃ Extrudates

2 kgs of alumina and 2 kgs of water were mixed for 20 minutes in a Z-type kneader mixer. The resultant paste was extruded through a 2-mm strainer of a single-screw 35 extruder and then was dried and calcined onto the desired surface.

Preparation of γ -Al₂O₃ Granules

Alumina and water were continuously mixed in a double-screw extruder at a feed rate of 15 kgs/h. The resultant granules were dried and then calcined onto the desired surface.

Examples 1 through 5**Dehydration of Hexanol on Alumina**

(for the specification, see Table II)

10

In a continuously operated tube reactor (23 mm in diameter, 100 mm in length), 2 ml/min of hexanol vapour having a purity of 99.4 % and 0.25 l/min of nitrogen were passed at 300 °C/325 °C and 2 bar through a 50-mm catalyst bed comprised of 7.2 to 9.9 grams of catalyst, depending on the bulk density.

15

When using the monomodal γ -alumina of Südchemie (CS 331-1; pore volume 0.82 ml/g) at 300°C reaction temperature, the organic phase obtained after phase separation of the crude product comprised 44.2 % hexanol, 32.2 % dihexyl ether, and 20.7 % 1-hexene (comparative example 4). The α -selectivity was 96.5 %.

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When using PURAL™ KR1 at 300°C reaction temperature, the organic phase obtained after phase separation of the crude product comprised 35.2 % hexanol, 38.7 % dihexyl ether, and 24.5 % 1-hexene. The α -selectivity of the hexenes was 97.7 %.

25

Table II
Gas-Phase Dehydration of 1-Hexanol on Al₂O₃ Catalysts

Examples	1	2	3	4	5	
Catalyst Al ₂ O ₃	CS 331-1 (Südchemie)	PURAL KR1 (Sasol)	PURAL KR1 (Sasol)	PURAL KR2 (Sasol)	P180 (Sasol)	
Type	Extrudates	Granules	Extrudates	Extrudates	Extrudates	
Surface (m ² /g)	235	184	232	215	157	
Pore volume (Hg) [ml/g], thereof pore radii of	0.83	1.31	1.28	0.89	0.99	
< 300 Å	0.69 (83%)	0.79 (60%)	0.77 (60%)	0.84 (94%)	0.77 (78%)	
300 – 1,000 Å	0.04 (5%)	0.05 (4%)	0.03 (2%)	0.01 (2%)	0.03 (3%)	
> 1,000 Å	0.09 (11%)	0.47 (36%)	0.48 (38%)	0.04 (4%)	0.19 (19%)	
Pore radius maximum > 1,000 Å	1,000	2,500	5,000	-	≈ 5,000 (large dis- tribution)	
Pore radius maximum < 1,000 Å	50	68/49	50/35	70/40	117	
Temperature [°C]	300	325	300	325	325	325
Feed quantity [ml/min]	2	2	2	2	2	2
Composition [wt%]						
1-Hexanol (educt 99.40)	44.22	24.77	35.21	19.03	21.14	21.83
Dihexyl ether	32.23	14.78	38.65	18.75	15.40	14.33
1-Hexene	20.704	52.551	24.517	58.421	58.840	58.653
cis-2-Hexene	0.518	4.210	0.412	1.839	2.320	2.668
trans-2-Hexene	0.180	1.483	0.116	0.530	0.826	1.007
cis-3-Hexene	0.013	0.118	0.010	0.046	0.066	0.085
trans-3-Hexene	0.011	0.103	0.008	0.037	0.056	0.076
2-Ethyl-1-butene	0.013	0.015	0.016	0.025	0.024	0.022
3-+4-Methyl-1-pentene	0.003	0.009	0.003	0.008	0.009	n. a.
3-Methyl-2-pentene	0.003	0.012	0.002	0.009	0.008	0.010
Total of other hexenes	-	-	-	-	-	0.31
Total of C ₆ olefins	21.45	58.50	25.08	60.92	62.15	62.53
Conversion [%]	55.52	75.08	64.58	80.86	78.74	78.04
α-Selectivity [%]	96.54	89.83	97.74	95.91	94.68	93.80
						91.21

Patent Claims

1. A process for producing α -olefins by dehydration of alcohols in the presence of γ -alumina,
5 characterised in that the alcohol is brought into contact with at least one γ -alumina having
 - a pore volume of greater than 0.9 ml/g,
 - at least one pore radii maximum in the mesopores range from 20 to 90
 - 10 \AA , and
 - at least one pore radii maximum in the macropores range, i.e. greater than 250 \AA .
2. The process according to claim 1,
15 characterised in that the pore volume of the mesopores in ml/g (pore radii from 10 to 250 \AA) of the γ -alumina makes up more than 40 % of the total γ -alumina pore volume.
3. A process according to any one of the preceding claims,
20 characterised in that the pore volume of the macropores in ml/g (pore radii greater than 250 \AA) of the γ -alumina makes up more than 20 % of the total γ -alumina pore volume.
4. A process according to any one of the preceding claims,
25 characterised in that the pore volume of the mesopores (pore radii from 10 to 250 \AA) of the γ -alumina is greater than 0.6 ml/g.
5. A process according to any one of the preceding claims,
30 characterised in that the pore volume of the macropores (pore radii greater than 250 \AA) of the γ -alumina is greater than 0.3 ml/g.
6. A process according to any one of the preceding claims,
characterised in that the γ -alumina comprises more than 99 wt% Al_2O_3 .
- 35 7. A process according to any one of the preceding claims,
characterised in that the dehydration is performed at temperatures ranging from 260 to 350 $^{\circ}\text{C}$, preferably 280 to 320 $^{\circ}\text{C}$.

8. The process according to any one of the preceding claims, characterised in that the alcohol employed herein is a linear alcohol, preferably at least one linear alcohol selected from the group consisting of 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 1-tridecanol and 1-tetradecanol.
9. A process according to any one of the preceding claims, characterised in that the alcohol employed herein is comprised of one or more 1-alkanol(s) having 4 to 14 carbon atoms, particularly 6 to 8.
10. A process according to any one of the preceding claims, characterised in that the γ -alumina is employed in the form of blanks, preferably as beads, pellets, extrudate, or granules, and independently thereof preferably in a fixed-bed reactor.
11. A process according to any one of the preceding claims, characterised in that the alcohol is in the gas phase when contacted with the γ -alumina.
12. A process according to any one of the preceding claims, characterised in that the dehydration is performed at a pressure of 10 to 2,000 mbar.
13. A process according to any one of the preceding claims, characterised in that the dehydration is continuously performed in a tube reactor.
14. A process according to any one of the preceding claims, characterised in that at least one pore radii maximum is found in the macropores range with pore radii of greater than 1,000 \AA .
15. The use of any one of the γ -aluminas claimed in any one of the preceding claims as a dehydration catalyst.

Fig. 1
Incremental Pore Volume

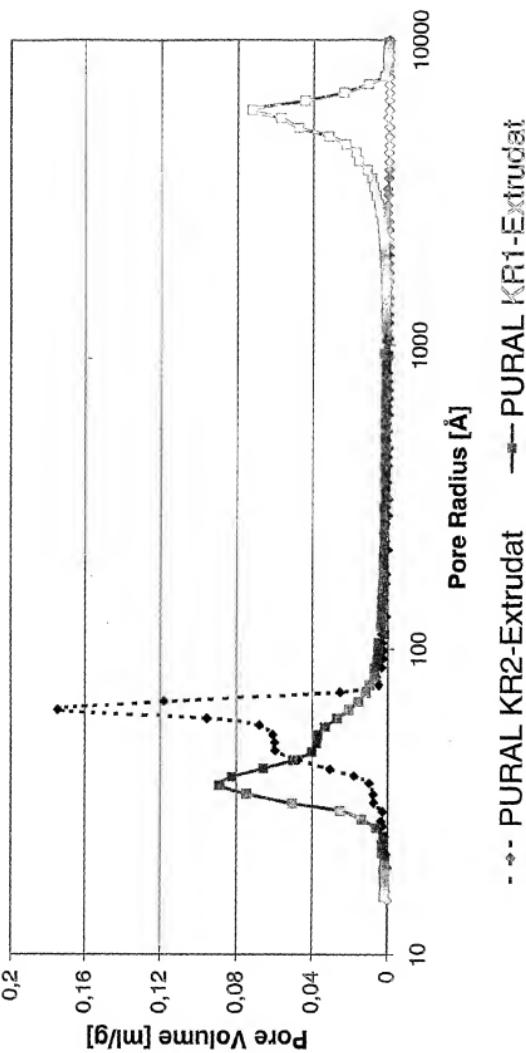


Fig. 2